The Systematic Analysis of Silicate Rocks using Ion Exchange Resin

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The many varieties of rock-forming-elements have necessitated the repetition of cycles of absorption and elution, which requires much time and effots for the analysis of silicate rocks using ion exchange resin[1,2]. In order to analyze many samples of ordinary silicate rocks, the present authors have developed a rapid and simple method of analysis using an ion exchange column and a solvent extraction technique. A complete analysis of an ordinary rock or silicate mineral can be carried out in only 3 days by this method.

Experimental

Chemicals and Ion Exchange Resin.—Amberlite IR-120 in 100~150 mesh was employed. The column was 18 cm. long and 1 cm. in diameter. The flow rate was 1 ml. per minute. Fractions were collected every 20 ml.

Constant boiling hydrochloric acid was used as 6 N acid.

Guaranteed-grade chemicals and distilled water were used.

Procedure.—*Decomposition.*—The analytical procedure is schematically illustrated in Fig. 1.

Weigh 100 mg. of the fine powder of the rock sample into a platinum dish, then add a few milliliter of water and dilute hydrofluoric acid. Mix and heat the dish on a sand bath, carefully at first, then more strongly, until fumes of sulfuric acid are given off. Cool, wash the side of the dish with a little water, and add 2 ml. of 1 : 1 sulfuric acid and 5 ml. of hydrofluoric acid. Evaporate again to dryness. Add 20 ml. of 6 N hydrochloric acid and warm until all soluble materials have been taken into solution. Remove the solution into a quartz dish. Cover with a watch glass, add 3 ml. of 3% hydrogen peroxide, and boil gently for a minute or two. After washing the watch glass with a little water, evaporate the solution to less than 10 ml.

Extraction Separation of Iron.—Cool the solution and transfer it to a 50 ml. separatory funnel. Make the solution less than 20 ml. and adjust the concentration of hydrochloric acid to 6 N hydrochloric acid. Shake thoroughly for two minutes. Allow the layers to settle and then separate the two layers. Repeat the extraction twice, and collect the ether layer containing iron in another separatory funnel. Strip the ferric iron into 10 ml. of water. Repeat stripping with 5 ml. of water. Transfer the aqueous layer into a 200 ml. Erlenmeyer flask and add 3 ml. of 6 N hydrochloric acid and 50 ml. of water. After gently boiling the aqueous solution to expel the ether, determine the total iron by the Zimmermann-Reinhard method.

Chromatographic Separation of Elements.—Evaporate the sample solution from which iron had been removed by extraction nearly to dryness (1~2 ml.). Care should be taken not to evaporate the contents; otherwise, titanium will be lost as insoluble materials to water. Add 20 ml. of water and pass through the column.

Pass 160 and 150 ml. of 0.4 N hydrochloric acid through the column to elute the sodium and potassium successively. Pass another 10 ml. of 8 N sulfuric acid for the detection of titanium by the hydrogen peroxide-sulfuric acid method. When no titanium is present, add the fraction to the effluent containing potassium and determine the sodium and potassium by flame photometry.

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1) J. Yoshimura and H. Waki, *Japan Analyst*, **6**, 362 (1957).

2) E. Minami, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 740 (1953).

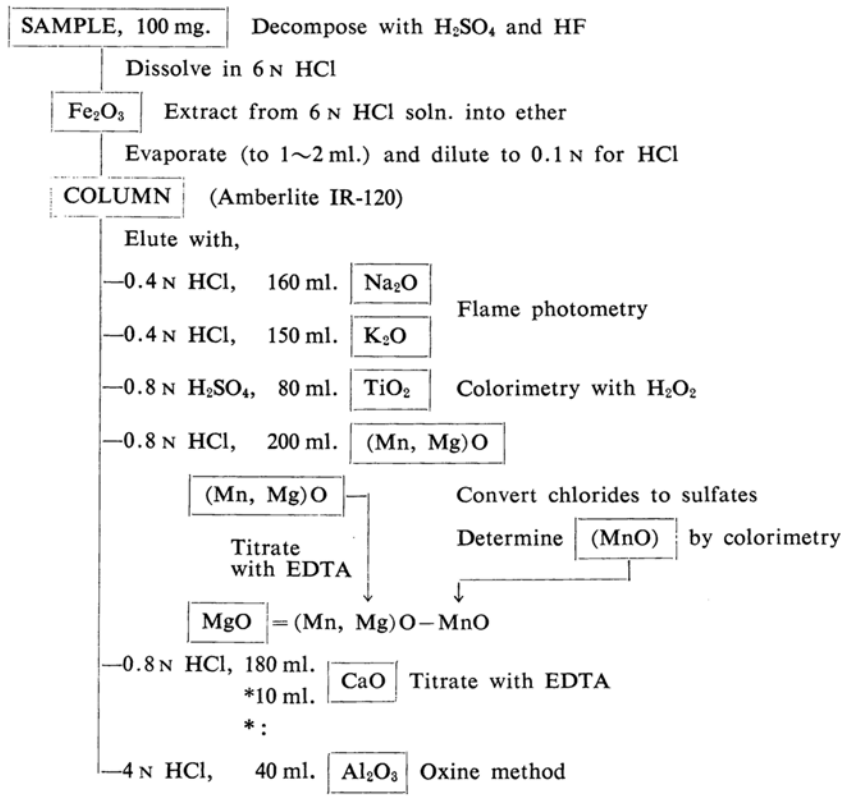

Fig. 1. The scheme of the analytical procedure.

* Detect Al with alizaline-S.

Table I. Ionic radius of rock forming elements

Element	Na	K	Ti(IV)	Mg	Fe(II)	Mn(II)	Ca	Fe(III)	Al
Ionic radius, Å[4].	0.98	1.33	0.68	0.78	0.83	0.91	1.06	0.67	0.57

Liberate the titanium with 70 ml. of 0.8 N sulfuric acid. Add 10 ml. of 1 : 1 sulfuric acid and 5 ml. of 3% hydrogen peroxide to the effluent and dilute the solution to 100 ml. in a volumetric flask. Determine the titanium by measuring the transmittancy of the solution at 420~430 mμ.

Pass 200 ml. of 0.8 N hydrochloric acid to elute the magnesium and manganese. Divide this effluent into two parts, and with the one part titrate the mixture of magnesium and manganese by the EDTA method. To the other part of the effluent, adding a few drops of dilute sulfuric acid to convert the chlorides into sulfates, evaporate it nearly to dryness. Determine the manganese colorimetrically by the permanganate method.

Elute the calcium by the 0.8 N hydrochloric acid. Test the absence of calcium in the first 40 ml. fraction. To make sure, pass fractionally 80, 40 and 20 ml. of 0.8 N hydrochloric acid. Determine the calcium for each fraction by the EDTA (Mg-EDTA) method. Ditect the aluminum with alizaline-S in each following 10 ml. fraction. When no aluminum is present, titrate the calcium.

Elute the aluminum with 40 ml. of 4 N hydrochloric acid. Evaporate the effluent nearly to dryness, and add 30 ml. of water. Warm at 70°C and add an excess of 8-hydroxyquinoline, and determine the aluminum by gravimetry.

Determination of Silica and Phosphorus.—Determine the silica by the ordinary gravimetric method by sodium carbonate fusion.

To determine phosphorus, take out one portion of the filtrate. The solution will conveniently contain less than 10 p. p. m. of phosphorus. Dilute with water, and pass through the column. Pass 50 ml. of 0.1 N hydrochloric acid to liberate the phosphorus completely. Evaporate the effluent nearly to dryness, and determine the phosphorus colorimetrically by the heteropoly-blue-method.

Discussion

Until recently, for the total analysis of a silicate rock, a long column or a set of columns consisting of two or more of them has been required. Aiming at simplicity and rapidity, the present authors adopted a short column (18 cm. long and 1 cm. in diameter) and constant-boiling hydrochloric acid as 6 N acid.

Titanium which is eluted with 0.8 N sulfuric acid as in Fig. 2 could also be eluted with 0.8 N hydrochloric acid. In this case, 0.8 N sulfuric acid is preferable for the colorimetric determination of titanium with hydrogen peroxide.

Following Sweet et al., a long column was used for the separation of the sodium and potassium with 0.7 N hydrochloric acid[3]. The present authors obtained good results with 0.4 N hydrochloric acid as shown in Fig. 2 with

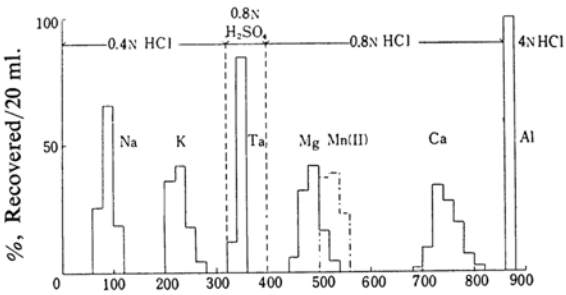

Fig. 2. Chromatographic separation of rock forming elements.

such a short column. Hydrochloric acid over 0.6 N causes the cross contamination of sodium (not shown).

Except for titanium, the order of elution is proved to be the order of increase in valence, and at constant valence, the order of increase in ionic radious (Table I).

Magnesium(II) and iron(II) and manganese-(II) are eluted with 0.8 N hydrochloric acid in almost the same position, as is shown in Fig. 2. The ionic radii of these ions are 0.78 for magnesium(II), 0.83 for manganese(II), and 0.91 Å for iron(II) respectively[4]. The similar size of the ionic radii of these ions inevitably causes the cross contamination of them with

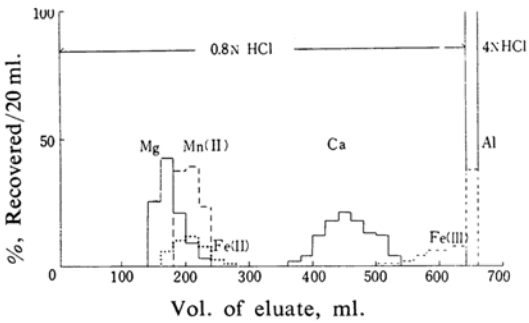

Fig. 3. Contamination of iron.

3) R. C. Sweet, W. Rieman, III, and J. Beukenkamp, *Anal. Chem.*, **24**, 952 (1952).
4) V. M. Goldschmidt, *Geochemische Verteilungsgesetze der Elemente*, **8**, 69 (1926).

Table II. Examples of analyses of standard samples

	Taken, mg.	Found, mg. 1	2	3
TiO_2	0.38	0.35	0.35	0.40
Al_2O_3	20.55	20.12	20.43	20.43
Fe_2O_3	5.93	5.85	5.88	5.87
MgO	2.03	2.00	2.10	2.08
MnO	0.20	0.19	0.22	n.d.
CaO	2.05	2.09	2.06	2.08
Na_2O	5.00	4.90	5.10	5.15
K_2O	5.00	4.80	4.72	4.90

Table III. The practical applications to a silicate rock

	Run 1 mg.	2 mg.	3 mg.	4 mg.
SiO_2	58.52			
TiO_2	0.91	0.90	0.91	0.90
Al_2O_3	16.40	16.35	16.75	16.31
Fe_2O_3	5.75	5.60	5.61	5.60
MnO	0.11	0.11	0.08	0.11
MgO	3.08	3.07	3.06	3.02
CaO	6.03	5.87	5.80	5.79
Na_2O	2.85	2.80	2.94	2.88
K_2O	2.33	2.44	2.41	2.33
H_2O	3.14			
H_2O	0.93			
P_2O_5	0.14			
Total	100.14			

Hypersthene andesite from Dogamori, Mt. Ishizuti, Ehime Prefecture (Collected by K. Horikoshi, Sp. No. 443). Note: FeO is calculated as Fe_2O_3. Analyst: K. Horikoshi, Y. Ôki.

such a short column. This disadvantage was overcome by the extraction of iron with ether before the chromatographic separation and by the respective determination of magnesium and manganese, as is shown in Fig. 1.

Aluminum and iron(III) are also eluted at the same time with 0.8 N hydrochloric acid (Fig. 3). This problem, however can be overcome by the extraction of the iron beforehand.

Titanium(IV) is hydrolyzed in dilute mineral acids to the titanyl ion. Accordingly, titanium should be ranked among the divalent ions.

Applicaton of this procedure was justified with the standard solution containing similar amounts of sodium, potassium, calcium, magnesium, manganese, iron, titanium and aluminum in 100~150 mg. of the ordinary igneous rocks (Table II). The practical applications of this method gave satisfactory results, which are summarized in Table III. A complete analysis of an ordinary rock sample can be carried out in only 3 days.

Summary

An accurate and rapid systematic analysis of ordinary silicate rocks was studied with a column of an ion exchange resin (Amberlite IR-120). A powdered rock sample was decomposed by the usual method of Berzelius. Iron was extracted from 6 N hydrochloric acid solution into ether before chromatographic separation Metal ions absorbed on the column are eluted as follows: With 0.4 N HCl Na and K, with 0.8 N H_2SO_4 Ti(IV), with 0.8 N HCl Mg, Mn(II), and Ca, and with 4 N HCl Al are eluted successively. A complete analysis of an ordinary rock sample can be carried out in only 3 days by this method.

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